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(54) Process for producing a hydrowax

(57) Process for producing a hydrowax comprising the steps of

- (a) hydrocracking a blend obtained by blending at least one distillate fraction and a deasphalted oil (DAO);
- (b) separating from the hydrocracker effluent a fraction of which at least 90% by weight has a boiling point of 370 °C or higher (the 370+ fraction); and

(c) separating the 370+ fraction in a top-fraction and a bottom-fraction at an effective cutpoint below 600 °C, thus yielding the hydrowax as the top-fraction.

The hydrowax thus produced is a very suitable feedstock for a steam cracker for the production of ethene. The hydrowax can also be very suitably applied as a feed for the production of lubricating base oils.

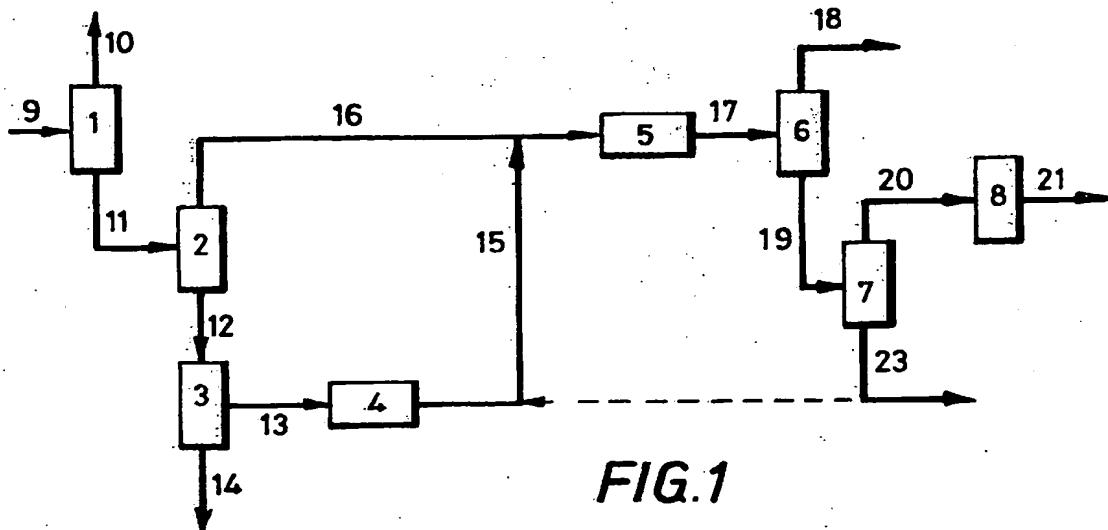


FIG.1

Description

The present invention relates to a process for producing a hydrowax which is very useful as a feedstock for a thermal steam cracker to produce lower olefins and as a feedstock for producing lubricating base oils.

Thermal steam cracking is a known method for producing lower olefins, particularly ethene and to a somewhat lesser extent propene. It is a strongly endothermic process and basically involves heating a hydrocarbon oil feed to a sufficiently high temperature for cracking reactions to occur followed by rapid cooling of the reactor effluent and fractionation of this effluent into the different products. A steam cracker, also commonly referred to as an ethene cracker, usually consists of a hot section and a cold section. The hot section consists of cracking furnaces, a cooling section and a primary fractionator for separating the effluent in a cracked residue, pan oil, cracked gas oil and cracked gas. Steam is introduced into the cracking furnace to dilute the feed. This is favourable for the final olefin yield, while the added steam also suppresses the deposition of coke in said furnace. In the cold section the cracked gas is further separated into the various end products among which are pure ethene and propene. In general, this separation is achieved by first compressing the cracked gas from the primary fractionator to a pressure of about 30-40 bar followed by cooling the compressed gas to temperatures below -100 °C to enable separation into the various pure end products. The removal of gases such as carbon dioxide and hydrogen sulphide also takes place in the cold section of the steam cracker. Because of the strong endothermic nature of the steam cracking process adequate and efficient heat recovery is very important in order to make the process economically viable.

A well known feedstock for the steam cracker is the naphtha fraction produced in the processing of crude oil. Atmospheric gas oils are also known as suitable cracker feedstocks. For instance, in British patent specification No. 1,537,822 a process for the production of lower olefins is disclosed involving the steam cracking of a hydrogenated gas oil feedstock, which is formed by the subsequent steps of thermal cracking of a hydrocarbon oil residue -suitably an atmospheric residue-, recovering a gas oil fraction by distillation from the thermal cracking effluent and catalytic hydrogenation of said gas oil fraction. In German offenlegungsschrift No. 1,922,665 a steam cracking process for preparing olefins is disclosed, wherein a dearomatised gas oil is used as the feedstock. Important considerations in respect of the choice of the feedstock are, beside the potential ethene yield, chemical factors like the H/C ratio of the feed as well as economic factors such as the price of the feedstock and the stability of this price on the market. Other factors such as availability of the feedstock, synergy potential of a steam cracker and a refinery and investments involved with integration of a steam cracker in a refinery also play an important role in choosing the appropriate feedstock.

5 Since the early eighties another feedstock has been used on a commercial scale. In the publication of A.G. Goossens, Hydrocarbon Processing, November 1986, pp. 84-86 it is described that the hydrowax, i.e. the hydrogenated residue, as produced by single-stage hydrocracking of flashed distillates is suitable as a feedstock for a steam cracker to produce ethene. The term "flashed distillates" as used in this context refers to the distillate fractions obtained in the vacuum flash distillation of atmospheric residue. It is described that hydrowax is an excellent steam cracker feedstock, inter alia because it has an attractive and relatively constant price, olefin yields are close to those for naphtha feedstocks and it offers excellent possibilities for integrating a steam cracker with a refinery. In said publication it is furthermore described that fouling of the transfer line heat exchanger or TLE, where high enthalpy heat is recovered from the hot effluent of the furnace for producing high pressure steam, is the major factor determining the run length of the steam cracker. This fouling is stated to be caused by the content of aromatic compounds in the hydrowax and by the tars formed during the pyrolysis in the cracking furnace. Since hydrowax tends to cause more TLE-fouling than the conventionally used naphtha feeds, specific measures have to be taken to cope with this fouling so that it does not seriously limit the run time. Quench pipe diameters in the TLE and maximum design and operating TLE outlet temperature are important variables in this respect.

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separated into a lower boiling fraction and a lubricating base oil raffinate, the latter being advantageously subjected to an aromatics extraction step, optionally followed by a hydrofinishing step, to yield the lubricating base oil.

The present invention also aims to provide a process wherein a hydrowax is prepared which can be very suitably used as a feedstock for producing lubricating base oils. Accordingly, the present invention aims to provide a process, wherein the hydrowax prepared is a suitable feedstock for a dewaxing unit or a hydroprocessing unit.

Accordingly, the present invention relates to a process for producing a hydrowax comprising the steps of

- (a) hydrocracking a blend obtained by blending at least one distillate fraction and a deasphalted oil (DAO);
- (b) separating from the hydrocracker effluent a fraction of which at least 90% by weight, preferably at least 95% by weight, has a boiling point of 370 °C or higher (the 370+ fraction); and
- (c) separating the 370+ fraction in a top-fraction and a bottom-fraction at an effective cutpoint below 600 °C, suitably below 580 °C, thus yielding the hydrowax as the top-fraction.

Because of the negative impact heavy metals usually have on the activity of hydrocracking catalysts, the blend of DAO and distillate fraction(s) should have a sufficiently low heavy metal content. It is therefore preferred that the heavy metal content of the hydrocracker feedstock has been reduced prior to hydrocracking. This implies that either the DAO is hydrodemetallised before being blended with the distillate fraction(s) or the blend of DAO and distillate fraction(s) is hydrodemetallised prior to being subjected to hydrocracking. In practice the first option, i.e. hydrodemetallisation of the DAO will be preferred, because all or almost all of the heavy metal present in the blend of DAO and distillate fraction(s) was originally contained in the DAO anyway, so that it is economically more effective to hydrodemetallise the DAO. In deciding whether or not a hydrodemetallisation step is actually required, there are two major factors. Firstly, the type of crude oil from which the DAO has been derived and secondly the depth at which the deasphalting treatment has taken place, i.e. the extent to which asphaltenic components are removed. In case the DAO has been derived from a crude oil in which heavy metals are naturally occurring in relatively high amounts, the DAO is likely to have a high heavy metal content as well. Additionally, if the deasphalting depth in the deasphalting treatment is high, i.e. only the most heavy asphaltenic components are removed, then the DAO will still contain substantial amounts of heavy metals as compared with the deasphalting feed. If, on the other hand, said depth is relatively low, i.e. beside the heavy asphaltenic components some lighter asphaltenes have been removed as well, then the heavy metals content in the DAO will be significantly lower than the heavy metals content of the

deasphalting feed and a separate demetallisation step can be dispensed with.

It is very surprising that a relatively heavy fraction such as a hydrodemetallised deasphalted oil can be used for preparing a hydrowax which is a suitable feedstock for a steam cracker. Up to now it was generally believed that the hydrowax should be produced from flashed distillate fractions only, since the use of heavier fractions would cause too much fouling in the TLE, thus imposing an economically unacceptable run time constraint on the steam cracker. It has now been found that by flashing the 370+ fraction obtained from hydrocracking a blend of flashed distillate and optionally demetallised DAO at an effective cutpoint in the range of from 400 to 600 °C, the hydrowax obtained as the top-fraction can very suitably be used as the feedstock for a steam cracker in order to produce ethene and propene or as a feedstock for a dewaxing or hydroprocessing unit for producing lubricating base oils.

The blending or weight ratio of distillate fraction(s) to DAO, which optionally has been hydrodemetallised, is not particularly critical and is primarily determined by hydrocracker constraints. Thus, this weight ratio is suitably in the range of from 20/80 to 80/20 and preferably from 40/60 to 70/30.

Hydrocracking of the blend of distillate fraction(s) and optionally hydrodemetallised DAO may be performed in any suitable way known in the art. Generally, hydrocracking is carried out in the presence of hydrogen and a suitable hydrocracking catalyst at elevated temperature and pressure. Hydrocracking catalysts usually consist of one or more metals from nickel, tungsten, cobalt and molybdenum in elemental, oxidic or sulphidic form on a suitable carrier such as alumina, silica, silica-alumina or a zeolite. There are many commercially available hydrocracking catalysts, which can be suitably applied in the process according to the present invention. For the purpose of the present invention the hydrocracking process can be a single- or a multiple-staged process, whereby a single-staged process is preferred because multiple-staged hydrocracking causes deeper hydrogenation of polycyclic aromatics, thus producing more polynaphthalenes. Such polynaphthalenes produce more fuels and tar and less olefins than a hydrowax resulting from a single-stage hydrocracking process. In the case of a single-staged process, a stacked bed of a hydrodenitrification/first-stage hydrocracking catalyst on top of a conversion catalyst can suitably be used. Particularly suitable hydrodenitrification/first-stage hydrocracking catalysts are NiMo/alumina and CoMo/alumina, optionally promoted with phosphorus and/or fluorine. Suitable conversion catalysts include those based on a Group VIB metal, a Group VIII metal and an acidic carrier. A promoter in the form of phosphorus (P) may be present as well. Concrete examples of such catalysts are NiW/zeolite, NiW/silica-alumina and NiW/zeolite/silica-alumina. Common hydrocracking conditions are an operating pressure of 80-250 bar, suitably 100-200 bar, and

an operating temperature of 300-500 °C, suitably 350-475 °C.

The distillate fractions useful in the process of the present invention may be either heavy gas oil fractions obtained from the atmospheric distillation of a crude oil or flashed distillate fractions obtained from the vacuum flash distillation or vacuum distillation of an atmospheric hydrocarbon oil residue. For the purpose of the present invention it is not strictly required to use sharply defined distillate fractions (such as obtained in vacuum distillation) and therefore it is preferred that the distillate fractions are produced by the less expensive vacuum flash distillation of an atmospheric hydrocarbon oil residue.

The DAO used is suitably obtained by deasphalting a residual hydrocarbon oil, preferably a vacuum residue. The deasphalting may be carried out in any conventional manner. A well known and suitable deasphalting method is solvent deasphalting, which involves the countercurrent treatment of the residual hydrocarbon oil feed with an extracting solvent. This extracting solvent usually is a light hydrocarbon solvent containing paraffinic compounds having 3 to 8 carbon atoms, such as propane, butane, isobutane, pentane, isopentane, hexane and mixtures of two or more of these. Preferred paraffinic hydrocarbons are those having 3 to 5 carbon atoms with butane, pentane and mixtures thereof being most preferred. The solvent deasphalting treatment is conveniently carried out in a rotating disc contactor or a plate column with the residual hydrocarbon oil feed entering at the top and the extracting solvent entering at the bottom. The lighter hydrocarbons present in the residual hydrocarbon oil dissolve in the extracting solvent and are withdrawn at the top of the apparatus. From this top-fraction, the DAO is obtained after recovery of the extracting solvent. The asphaltenes, which are insoluble in the extracting solvent, are withdrawn at the bottom of the apparatus. The conditions under which deasphalting takes place are known in the art. Suitably, deasphalting is carried out at a total extracting solvent to residual hydrocarbon oil ratio of 1.5 to 8 wt/wt, a pressure of 1 to 50 bar and a temperature of 160 to 230 °C.

Hydrodemetallisation of either the DAO or the blend thereof with distillate fraction(s) can be achieved by any hydrodemetallisation method known in the art. Usually, such method involves passing the feed to be treated in an upward, downward or radial direction through one or more vertically disposed reactors containing a fixed or moving bed of hydrodemetallisation catalyst particles at an elevated temperature and pressure in the presence of hydrogen. Well known demetallisation operations are the bunker flow operation, the fixed bed operation, the fixed bed swing operation and the movable bed operation. Suitable catalysts usually consist of oxidic carriers such as alumina, silica or silica-alumina, on which one or more metals of Group VIIB or VIII of the Periodic Table of Elements may be deposited either in elemental form or as a metal compound. Such hydrodemetallisation catalysts are commercially available from many catalyst suppliers. Particularly suitable catalysts are those having

as the active agent one of the combinations NiMo or CoMo, optionally promoted with phosphorus (P), on an alumina carrier. It is well known that the type of catalysts described hereinbefore in practice will also exhibit some upgrading activity in terms of hydrodenitration and/or hydrodesulphurization, removal of heavy hydrocarbons and conversion of hydrocarbons having a boiling point above 520 °C into components having a lower boiling point. Hydrodemetallisation is usually carried out at a hydrogen partial pressure of 20-250 bar, a temperature of 300-470 °C, preferably 310-440 °C, and a space velocity of 0.1-10 l/l.hr, preferably 0.2-7 l/l.hr.

For the purpose of the present invention, it is preferred that the DAO used is produced by deasphalting a vacuum hydrocarbon oil residue, optionally followed by hydrodemetallisation. Generally, a vacuum hydrocarbon oil residue is obtained as the residual fraction of the vacuum distillation of an atmospheric hydrocarbon oil residue. As already described above, the distillate fraction(s) used in the process according to the present invention are preferably obtained from the vacuum distillation of an atmospheric hydrocarbon oil residue as well. In a further preferred embodiment of the present invention said vacuum hydrocarbon oil residue from which the DAO is produced, is derived from the same atmospheric hydrocarbon oil residue as said distillate fraction(s). This preferred line-up is illustrated in Figure 1 and clearly shows that the process of the present invention for producing hydrowax offers a high synergy potential between a refinery and a steam cracker, when said hydrowax is used as a steam cracker feed. Similarly, a high synergy potential can be recognised when integrating the present process for producing hydrowax with a process line-up for producing lubricating base oils.

Separation of the 370+ fraction from the hydrocracker effluent (step (b)) can be achieved by means of fractionation devices commonly applied in hydrocracker units. The separation in step (c) can also be performed by any method known in the art for separating a hydrocarbon oil feed into two or more different fractions based on the boiling points of the various components present in said hydrocarbon oil feed. Examples of suitable separation methods include distillation at atmospheric or reduced pressure, such as conducted in a mid vacuum flasher or a high vacuum distillation unit. The only important parameter in this respect for the purpose of the present invention is the effective cutpoint, i.e. the temperature indicating the boiling point of the highest boiling components of the top-fraction and the lowest boiling components of the bottom-fraction. In practice this will mean that at least 85% by weight, preferably at least 90% by weight and most preferably at least 95% by weight, of the components constituting the top-fraction has a boiling point below the effective cutpoint, while at least 70% by weight of the components constituting the bottom-fraction has a boiling point above the effective cutpoint. As already indicated above the effective cutpoint must be below 600 °C and preferably below 580 °C. Preferably, the effective cutpoint is above 400 °C and more prefera-

bly above 450 °C. From a yield perspective, it will usually be even more preferred to use an effective cutpoint above 500 °C and most preferably above 550 °C, because -as will be generally appreciated- a lower effective cutpoint goes at the expense of the hydrowax yield. On the other hand, if it is the aim to have as little heavy hydro-carbonaceous components as possible in the hydrowax, a lower effective cutpoint should be chosen.

The hydrowax is eventually obtained in step (c) as the top-fraction and can be used directly as feed for a steam cracker or as feed for a process line-up for producing lubricating base oils. The bottom-fraction contains many heavy hydrocarbonaceous compounds, partly polycyclic aromatic ring-structures. In order to increase the efficiency of the hydrowax production, at least a part of the bottom-fraction obtained in step (c) may be blended with the optionally hydrodemetallised DAO prior to hydrocracking. In this way an optimum hydrowax yield can be realised. Additional efficiency increasing measures include for instance recycling at least a part of the cracked residue and/or the cracked gas oil fraction obtained from the steam cracker to the inlet of the deasphalter and/or to the inlet of the hydrodemetallisation reactor, if the DAO is hydrodemetallised.

The present invention also relates to the hydrowax obtainable by the process according to the present invention and to the use of this hydrowax both as the feed in thermal steam cracking for producing lower olefins and as the feed in the production of lubricating base oils.

Figure 1 illustrates how a preferred embodiment of the process according to the present invention can be integrated in a refinery-steam cracker line-up or in a refinery having lubricating base oil production facilities.

A crude oil (9) is passed into atmospheric distillation unit (1), where it is separated into atmospheric residue (11) and distillate fractions (10). The atmospheric residue (11) is subjected to vacuum flash distillation in vacuum flash distillation unit (2) and separated into one or more (vacuum) flashed distillate fractions (16) and vacuum residue (12). Vacuum residue (12) is subsequently passed into deasphalting zone (3) resulting in asphaltic fraction (14) and DAO (13), which is hydrodemetallised in hydrodemetallisation unit (4). The hydrodemetallised DAO (15) is blended with distillate fraction(s) (16) and the resulting blend stream is subjected to hydrocracking in hydrocracker (5). The hydrocracker effluent (17) is separated in fractionator (6) into top-fraction (18) and 370+ bottom-fraction (19). This 370+ fraction is separated in (high) vacuum distillation unit (7) into hydrowax (20) and bottom-fraction (23), part of which may be blended with hydrodemetallised DAO (15). This is indicated with a dotted line. The hydrowax (20) is used as the feed for steam cracker (8), thus producing ethene (21). Alternatively, the hydrowax (20) is used as the feed for lubricating base oil production facility (8), thus producing lubricating base oil(s) (21).

The invention is further illustrated by the following example.

Example

A flashed distillate FD having the properties as listed in Table I was blended with a hydrodemetallised DAO (DAO+) in a weight ratio of FD:DAO+ of 55:45. The DAO+ was obtained by passing a DAO (obtained by subjecting vacuum residue to butane deasphalting at 70 %wt yield; properties listed in Table I) over a conventional hydrodemetallisation catalyst (NiMoP on alumina) under the conditions specified in Table II. The resulting FD/DAO+ blend was subjected to hydrocracking over a stacked bed of a conventional first stage hydrocracking catalyst (NiMoP on alumina) on top of a dedicated second stage hydrocracking catalyst (NiW on amorphous silica-alumina) under the conditions listed in Table II. The hydrocracker effluent was separated in a fractionator into a top-fraction and a 370+ bottom-fraction. This 370+ fraction was then separated in a vacuum flasher at an effective cutpoint of 576 °C into a hydrowax (the top fraction) and a bottom fraction. The properties of the hydrowax are also given Table I.

The hydrowax was subsequently passed into a steamcracking unit. The steamcracking unit was operated at a temperature of 820 °C, an outlet pressure of 2.15 bar, a feed flow of 49.6 g/h and a gas flow of 43.8 Nl/h. Ethene yield was 28.0 %wt and propene yield was 13.8 %wt, bath weight percentages being based on weight of feed.

TABLE I

Properties of FD, DAO and hydrowax			
	FD	DAO	Hydrowax
Carbon (%wt)	86.1	86.4	85.8
Hydrogen (%wt)	12.4	12.2	14.2
Sulphur (%wt)	1.1	1.4	0.02
Nitrogen (mg/kg)	1200	4200	18.9
IBP (°C)	298	396	346
10 %wt (°C)	362	516	402
30 %wt (°C)	408	580	427
50 %wt (°C)	439	634	451
70 %wt (°C)	465	692	483
90 %wt (°C)	528	736	540
96 %wt (°C)	-	-	570
FBP (°C)	>620	>740	616

TABLE II

Process conditions		
	HDM	HCU
Total Pressure (bar)	171.3	171.3
WHSV (kg/l/h)	0.6	0.6
Gas rate (NI H ₂ /kg)	1000	2000
Temperature (°C)	350	389

Claims

1. Process for producing a hydrowax comprising the steps of

- (a) hydrocracking a blend obtained by blending at least one distillate fraction and a deasphalted oil (DAO);
- (b) separating from the hydrocracker effluent a fraction of which at least 90% by weight has a boiling point of 370 °C or higher (the 370+ fraction); and
- (c) separating the 370+ fraction in a top-fraction and a bottom-fraction at an effective cutpoint below 600 °C, thus yielding the hydrowax as the top-fraction.

2. Process according to claim 1, wherein the DAO is hydrodemetallised before being blended with the distillate fraction(s).

3. Process according to claim 1 or 2, wherein the weight ratio distillate fraction(s) to optionally hydrodemetallised DAO in the blend to be hydrocracked is in the range of from 20/80 to 80/20 and preferably from 40/60 to 70/30.

4. Process according to any one of the preceding claims, wherein the distillate fraction(s) are produced by vacuum flash distillation of an atmospheric hydrocarbon oil residue.

5. Process according to any one of the preceding claims, wherein the DAO is produced by deasphalting a vacuum hydrocarbon oil residue.

6. Process according to claims 4 and 5, wherein the vacuum hydrocarbon oil residue of claim 5 is produced from the same atmospheric hydrocarbon oil residue as the distillate fraction(s) of claim 4.

7. Process according to any one of the preceding claims, wherein the effective cutpoint in step (c) is in the range of 400 to 560 °C, preferably 450 to 520 °C.

8. Process according to any one of the preceding claims, wherein at least a part of the bottom-fraction obtained in step (c) is blended with the optionally hydrodemetallised DAO prior to hydrocracking.

9. Hydrowax obtainable by the process of any one of claims 1 to 8.

10. Use of the hydrowax of claim 9 as a feed in thermal steam cracking for producing lower olefins.

11. Hydrocracker refinery integrated with a steam cracker, wherein the feed for the steam cracker is produced in the hydrocracker refinery operated according to the process of any one of claims 1 to 8.

12. Use of the hydrowax of claim 9 as a feed for the production of lubricating base oils.

13. Hydrocracker refinery integrated with a process line-up for producing lubricating base oils, wherein the feed for said process line-up is produced in the hydrocracker refinery operated according to the process of any one of claims 1 to 8.

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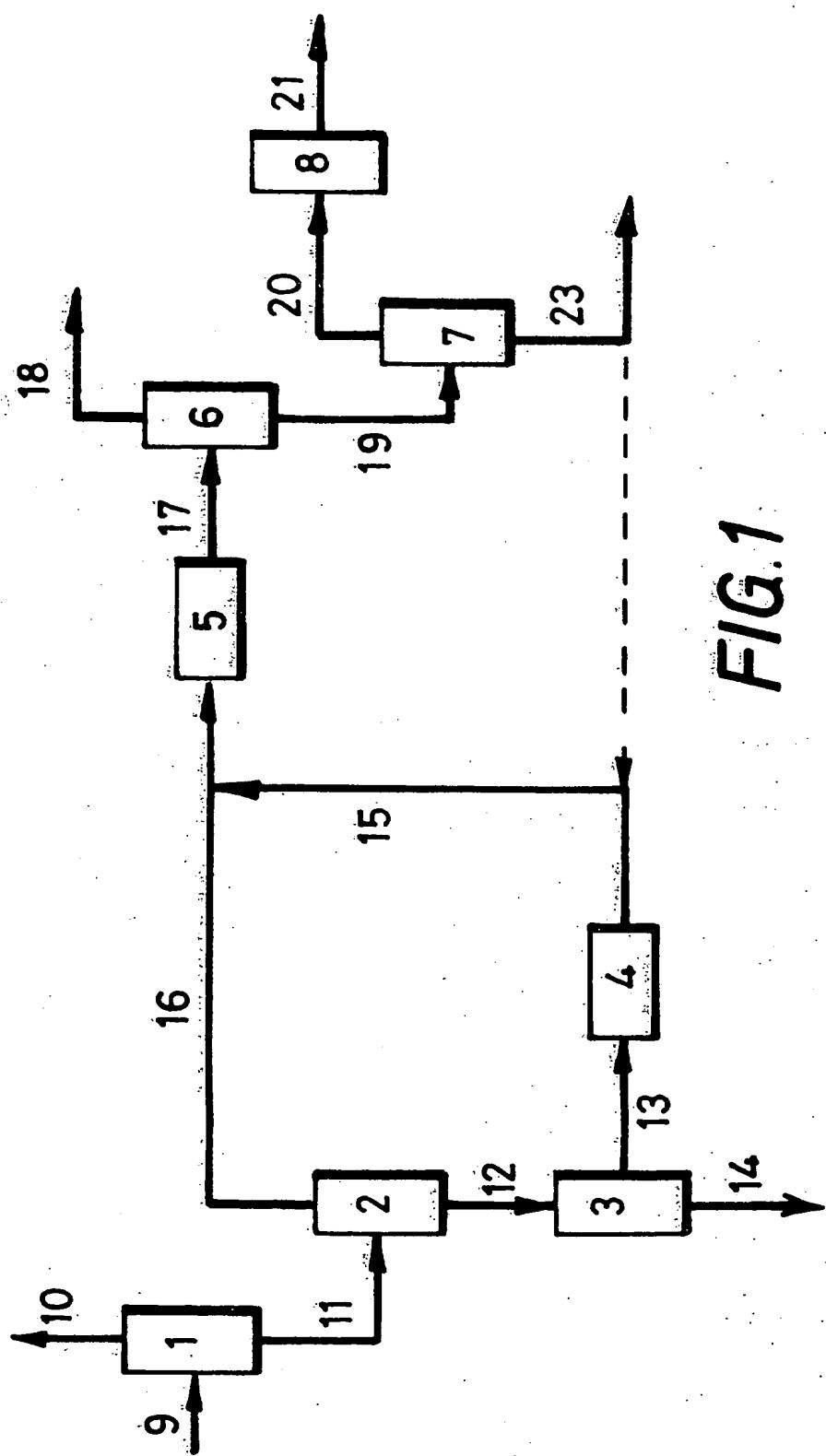


FIG. 1

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(54) Process for producing a hydrowax

(57) Process for producing a hydrowax comprising the steps of

(a) hydrocracking a blend obtained by blending at least one distillate fraction and a deasphalted oil (DAO);

(b) separating from the hydrocracker effluent a fraction of which at least 90% by weight has a boiling point of 370 °C or higher (the 370+ fraction); and

(c) separating the 370+ fraction in a top-fraction and a bottom-fraction at an effective cutpoint below 600 °C, thus yielding the hydrowax as the top-fraction.

The hydrowax thus produced is a very suitable feedstock for a steam cracker for the production of ethene. The hydrowax can also be very suitably applied as a feed for the production of lubricating base oils.

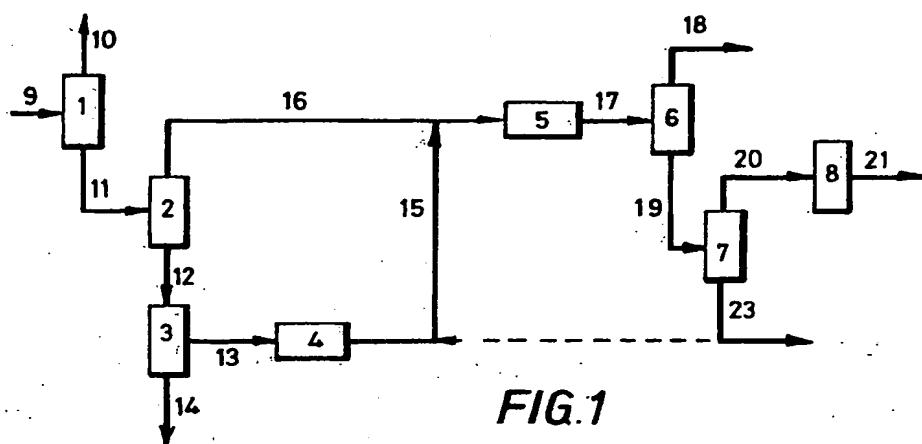


FIG.1



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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)						
A	EP-A-0 309 621 (UOP) * claims 1,5 * * figure 1 *	1,4-6	C10G67/04						
A	US-A-4 640 762 (GULF CANADA CO.) * claims 1,7 * * column 8, line 24 - line 45 *	1,5,9							
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TECHNICAL FIELDS SEARCHED (Int.Cl.6)									
C10G									
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>4 March 1996</td> <td>De Herdt, O</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	4 March 1996	De Herdt, O
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